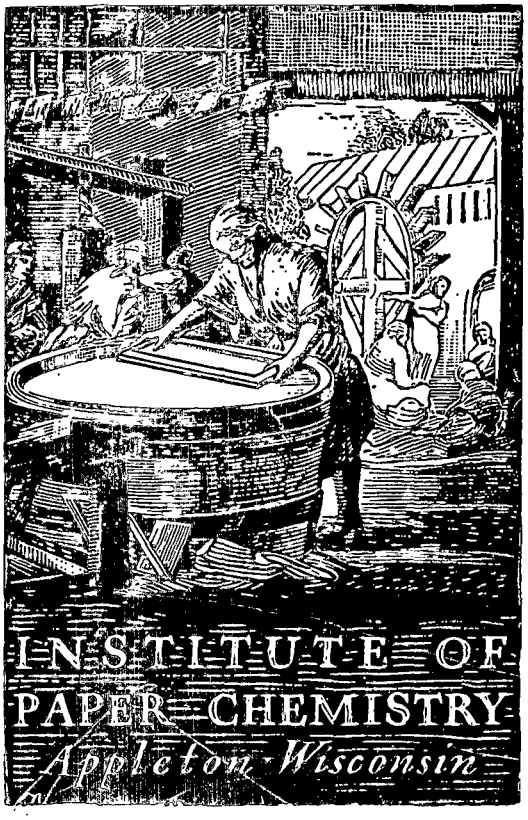

AN EVALUATION OF NONCONVENTIONAL CAUSTICIZING TECHNOLOGY FOR KRAFT CHEMICAL RECOVERY

Project 3473-3

Report One
A Progress Report
to
MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

January 30, 1981

THE INSTITUTE OF PAPER CHEMISTRY

APPLETON, WISCONSIN

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Appleton, Wisconsin

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SUMMARY

An evaluation was made of alternative causticizing technologies based on the use of amphoteric salts to release CO_2 from Na_2CO_3 directly in the furnace. The evaluation examined the chemistry of smelt decarbonization reactions and subsequent hydrolysis to assess the technical feasibility of closed process recovery technologies based on those reactions. In addition, comparative material and energy balances were carried out to focus on economic factors and operating conditions which would be involved.

Only two nonconventional causticizing technologies are technically feasible for kraft chemical recovery: autocausticizing with borate and smelt causticizing with titanates. Smelt causticizing with ferric oxide is a feasible technology for nonsulfur systems, but it cannot be used for kraft recovery because of the formation of insoluble FeS.

A borate autocausticizing system would operate with a steady-state inventory of borate throughout the system at a molar ratio Na:B slight greater than 2:1. The actual smelt decarbonizing agent would be $NaBO_2$. The $NaBO_2$ would effectively constitute an inorganic dead load in the entire pulping and recovery system.

The decomposition of Na_2CO_3 by borate is inhibited by the presence of CO_2 in the surrounding atmosphere. Since relatively large quantities of CO_2 could be present inside a recovery furnace, there are questions as to whether or not high carbonate conversion efficiencies could be obtained with borates during a

typical liquor burning operation. Further data are needed on this point before proceeding with the development of a borate based system. Conversion efficiencies of at least 80% are needed.

In the titanate system, the actual smelt decarbonizing agent is sodium trititanate ($Na_2Ti_3O_7$). This would be mixed with black liquor prior to firing in the furnace, with a molar ratio $Na_2O:TiO_2$ of about 1 in the smelt discharge. Dissolution of the smelt would result in precipitated $Na_2Ti_3O_7$ which would be recycled, and a strong caustic solution suitable as a white liquor.

The major difference between the borate system and the titanate system is that $NaBO_2$ is soluble in white liquor, while $Na_2Ti_3O_7$ is not. Thus the decarbonizing agent is always present in the liquor in the borate case and combustion of the liquor causes the sodium salts to self (auto) causticize. The titanate, on the other hand, precipitates from the white liquor and is recycled to the heavy black liquor as a solid product. Thus the titanate loop only intersects the sodium loop through combustion and smelt dissolution.

Economic factors (cheaper chemicals and less capital equipment requirements) favor the borate process over the titanate process. However, there are two technical factors which may make the borate process less attractive.

1. The borate process requires that the alkaline borate solution be used directly in pulping. This solution is not chemically identical to a NaOH solution, and there could be differences in pulping performance. If this should slow the pulping rate or impair pulp quality, the advantage would swing to titanate which produces a conventional white liquor. Pulping effects are not considered in this report.

2. If the presence of CO_2 in the reducing zone of the recovery furnace prevents conversion efficiencies of 80% from being obtained, the resulting increase in dead load inorganics and water in the system causes the economic advantage of borate to diminish rapidly.

On balance, a comparison between conventional causticizing with lime and nonconventional causticizing with borate or titanate appears to favor the lime system. There do not appear to be any overwhelming advantages to the nonconventional processes and some of the drawbacks are potentially very serious.

There is a marked increase in solids load and water load to the recovery furnace in both the borate and titanate systems. This will tend to lower combustion temperatures and could lead to combustion instability. Unstable or marginal combustion could result in a continuing need for auxiliary fuel to sustain combustion and could negate any advantage of eliminating the lime kiln fossil fuel requirement.

Comparative energy balance showed relatively little difference between conventional and nonconventional causticizing. The borate and titanate processes gave less steam generation from the recovery boiler and this was counterbalanced by the elimination of the lime kiln fossil fuel requirement. Other differences were minor.

Chemical make-up costs would be significantly higher with nonconventional causticizing because of the much higher unit cost of the chemicals. Titanate is worse than borate in this respect. Cost parity with conventional causticizing on make-up would require total recovery efficiencies much greater than those presently attained. With normal recovery efficiencies, excess make-up chemical costs could easily wipe out any other cost advantages of the nonconventional technologies.

Borate and titanate processes do show potential for capital cost savings over conventional causticizing. This benefit is most significant in a new mill

situation. The titanate system has a significant capital requirement itself for solids removal and handling equipment and this reduces any comparative advantage over the lime system. Borate autocausticizing requires little capital equipment per se, but the system is prone to capacity reductions in other parts of the process because of the large recirculating dead loads.

INTRODUCTION

In conventional alkaline chemical recovery, the Na_2CO_3 in the green liquor is causticized with lime to form NaOH and lime mud ($CaCO_3$). The lime mud can then be calcined to regenerate lime and close the lime cycle. The basic reactions are:

$$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3 \quad (1)$$

and

$$CaCO_3 \rightarrow CaO + CO_2 \quad (2)$$

The overall reaction can then be written as

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2 \quad (3)$$

The causticizing agent, CaO, functions essentially as a carrier for removing acidic CO_2 from Na_2CO_3 and thus converting it to the more alkaline NaOH.

These processes are required because Na_2CO_3 will not spontaneously decompose to Na_2O and CO_2 under normal furnace temperatures and gas concentrations. However, in the presence of certain amphoteric metal oxides or salts, molten Na_2CO_3 can be converted directly to Na_2O and CO_2 under furnace conditions. Dissolution of the resulting smelt in water yields caustic directly.

The chemistry of the decarbonization of Na_2CO_3 is illustrated as follows:

$$Na_2CO_3 + n\ M_xO_y \rightarrow Na_2O\cdot(M_xO_y)_n + CO_2 \quad (4)$$

or

$$Na_2CO_3 + Na_2\ M_xO_{y+1} \rightarrow Na_2O\cdot Na_2\ M_xO_{y+1} + CO_2 \quad (5)$$

where MxOy can be one of a number of amphoteric metal oxides such as B_2O_3, P_2O_5, SiO_2, Al_2O_3, TiO_2 and Fe_2O_3 (1).

There are basically two classes of decarbonizing agents; those whose reaction products are water soluble, and those whose are not.

When the reaction product is water soluble, the decarbonizing agent is carried through the entire pulping and recovery cycle as a caustic solution. Ultimately a steady state situation is obtained at some level of the amphoteric salt in the system. The amphoteric salt becomes the actual decarbonizing agent as in reaction (5) above. This type of process is referred to as autocausticizing, since the decarbonization of smelt is caused by the cooking chemicals themselves.

When the product of the decarbonizing reaction is not water soluble, the dissolution reaction can be written as;

$$Na_2O \cdot (M_xO_y)_n + H_2O \rightarrow 2NaOH + n\ M_xO_{y(s)} \qquad (6)$$

In this case the decarbonizing agent precipitates out of the resulting alkaline solution and can be recycled to the decarbonization step. It does not pass through the entire pulping and recovery system. Kiiskila (2) refers to this type of process as smelt causticizing, to distinguish it from the autocausticizing systems.

The smelt decarbonizing agents which were considered in this present study are listed and classified in Table I.

TABLE I

SMELT DECARBONIZING AGENTS

Autocausticizing (soluble)		Smelt Causticizing (insoluble)
$NaBO_2$	(B_2O_3)	TiO_2
$Na_2B_4O_7$		Fe_2O_3
$Na_4P_2O_7$	(P_2O_5)	$(FeO \cdot TiO_2)$ ilmenite
$Na_2Si_2O_5$	(SiO_2)	
Al_2O_3		

The main interest in smelt decarbonization is its potential for eliminating the lime system and causticizers from the alkaline recovery system. This would result in two main benefits:

1. Elimination of capital and operating costs associated with causticizing and calcining.
2. Elimination of the fossil fuel requirements for the lime kiln.

There are a number of other possible benefits associated with the effect of the decarbonizing agents on the burning process. These might ultimately lead to ways of increasing the capacity of existing recovery boilers.

A limited amount of information has been published on autocausticizing chemistry, effects on pulping, and aspects of recovery (1-18). However, there has been no published systematic study of the impact of autocausticizing on the complete pulping and recovery cycle. That is the purpose of this report.

The report objectives are as follows:

1. A summary of the basic chemisty involved in autocausticizing.
2. Definition of the impact of autocausticizing on the pulping process and the recovery system.
3. Identification of key leverage points.
4. Identification of critical information gaps needed to reach definitive conclusion on the feasibility of the approach.

GENERAL CHEMISTRY

SMELT DECARBONIZATION

The basic reaction in smelt decarbonizing is that between Na_2CO_3 and an amphoteric salt or metal oxide to drive off CO_2 from the Na_2CO_3. Amphoteric substances are those which are capable of reacting as either an acid or a base.

Lux has proposed a more precise acid-base definition for oxide systems (19), in which bases lose an oxygen ion to form acids.

$$\text{base} = \text{acid} + O^{2-} \qquad (7)$$

Some examples of this are:

$$OH^- = H^+ + O^{2-} \qquad (8)$$

$$Na_2O = 2Na^+ + O^{2-} \qquad (9)$$

$$TiO_3^{2-} = TiO_2 + O^{2-} \qquad (10)$$

On this basis then, the smelt decarbonization reaction can be considered as involving two distinct steps:

$$CO_3^{2-} = O^{2-} + CO_2\ (g) \qquad (11)$$

$$M_xO_y + O^{2-} = M_xO_{y+1}^{2-} \qquad (12)$$

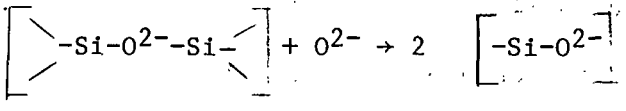
Flood and Forland (20) proposed that the characteristic process of acid-base reactions is a transfer of an oxygen ion from one state of polarization to another. For example the reaction between SiO_2 and carbonate to give silicate and CO_2 could be thought of as:

$$O_{CO_3}^{2-} + [SiO_2] \rightarrow O_{SiO_3}^{2-} + [CO_2] \qquad (13)$$

The system may be viewed as being composed of large oxygen ions and relatively small cations, with the state of polarization of the oxygen ion dependent on the surrounding cations.

Three types of acid-base transitions are possible in these systems:

1. Atoms of high ionization energy (S, C) frequently give acid-base transitions accompanied by an alteration in their coordination number for oxygen (e.g., reaction 11).
2. Atoms with medium ionization energy (B, Si) may give transitions in which the coordination number is unchanged. In these cases the acid-base transition consists of breaking an oxygen bridge between adjacent groups, e.g.,



(14)

3. Atoms with a low ionization energy (the typical cation forming ones) may undergo an acid-base transition connected with the formation of an oxide phase, e.g.

$$Mg^{2+} + O^{2-} \rightarrow MgO_{(s)} \qquad (15)$$

The essence of the above discussion is that the effectiveness of any particular smelt decarbonizing agent depends on its ability to compete with CO_2 for oxygen ions. The affinity of CO_2 toward O^{2-} in pure Na_2CO_3 melts is rather strong, since the decomposition of Na_2CO_3 to Na_2O and CO_2 does not proceed to an appreciable extent below 1000°C. An oxide with a greater attraction toward O^{2-} than CO_2 (a more acidic oxide) is needed to react with oxygen ion if CO_2 is to be expelled at lower temperatures. As the metal oxide reacts and removes oxygen ion from the system, it shifts the equilibrium toward CO_2 release. On this basis, one would expect more acidic metal oxides would be more effective decarbonizing agents.

SOLUTION CHEMISTRY

As mentioned previously, two different types of behavior can be obtained when the product of the smelt decarbonization reaction is dissolved in water:

1. The product may be completely soluble,

or 2. The product may react with water to form NaOH and precipitate the decarbonizing agent.

This behavior leads to an important restriction on the suitability of various decarbonizing agents for alkaline pulping and recovery.

Autocausticizing

Consider the soluble case (autocausticizing). The solution obtained after decarbonizing must be sufficiently alkaline to be effective for pulping. It should have an initial pH close to 14 and the pH should not fall below about 11.5 as the cook proceeds and alkali is consumed. Let NaA be a general representation of the salt produced by the decarbonizing reaction. The behavior of this salt during cooking can be analyzed by assuming that the salt undergoes hydrolysis to form NaOH, and that the resulting NaOH reacts with organic material during pulping.

$$NaA + H_2O = NaOH + HA \qquad (16)$$

and

$$NaOH + Org\ H = Org\ Na + H_2O \qquad (17)$$

Thus, the requirements for an autocausticizing agent, HA, include that NaA be nearly as alkaline as NaOH, (pH of 1N solution of about 14) and that HA itself have sufficient alkalinity (pH of a 1N solution of 11.5 to 12).

It should also be noted that the soluble (autocausticizing) systems have a high inherent load of chemicals inactive during pulping (dead load). The inorganic cycle can be represented as follows:

(decarbonization) $\frac{1}{2}Na_2CO_3 + HA \rightarrow NaA + \frac{1}{2}H_2O_{(g)} + \frac{1}{2}CO_{2(g)}$

(dissolution) $NaA + H_2O \rightarrow NaOH + HA$

(pulping) $NaOH + Org\ H \rightarrow Org\ Na + H_2O$

(combustion) $Org\ Na \rightarrow \frac{1}{2}\ Na_2CO_3$

The autocausticizing agent (HA) formed during dissolution (or by the acidification during pulping) is present throughout the system. Two parameters are needed to define the dead load in an autocausticizing system.

1. The degree of conversion of Na_2CO_3 during decarbonizing,
2. The ratio of autocausticizing agent to Na_2CO_3 before decarbonizing

Then,

$$(\text{Dead Load})_{AC} = \frac{(1-C) + S}{0.755\ C} \qquad (18)$$

where,

C = fractional conversion of Na_2CO_3

S = weight ratio of HA to Na_2CO_3 before decarbonizing.

The comparable dead load for the conventional process, causticizing with lime is

$$(\text{Dead Load})_{conv} = \frac{(1-C)}{0.755\ C} \qquad (19)$$

Although Eq. (18) and (19) are superficially very similar, the differences in dead load are not inconsequential. For example, for the conventional process at 80% conversion, the dead load is 0.33 lb Na_2CO_3/lb NaOH. For autocausticizing with a stoichiometric amount of $NaBO_2$, and an 80% conversion, the dead load is 2.39 lb/lb NaOH. This is seven times greater than the dead load with conventional causticizing.

Smelt Causticizing

A different set of problems exists for those systems in which the decarbonizing agent is insoluble in water. The relevant reaction is reaction 6,

$$Na_2O \cdot (M_xO_y)_n + H_2O \rightarrow 2NaOH + n\ M_xO_y\ (s)$$

Kiiskila has referred to this step as the hydrolysis step. If the decarbonization of Na_2CO_3 in the smelt is to have any ultimate usefulness, the Na_2O must be released from the metal oxide to form caustic.

The hydrolysis reaction does not necessarily go to completion. Some of the $Na_2O \cdot M_xO_y$ complexes which may form may be insoluble in water. In addition there may be accessability problems with the water having great difficulty penetrating the crystal structure to reach the Na_2O. The NaOH formed may require long periods of time to diffuse out of the solid matrix. Thus there may be kinetic limitations to hydrolysis as well.

The degree of completion of the hydrolysis step depends on a number of variables. The most important of these are listed below.

1. The specific metal oxide used
2. The ratio of M_xO_y to Na_2O
3. The temperature during hydrolysis
4. The retention time
5. The concentration of NaOH in the "white liquor"

The first two of these are primarily related to the formation of insoluble compounds, while the latter are related to mass transfer effects.

The formation of an insoluble sodium salt does not necessarily mean that a smelt causticizing process in unworkable. The key requirement is that the insoluble

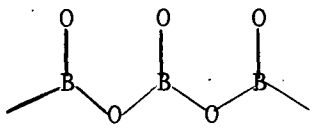
material must itself act as a decarbonizing agent [as in reaction (5)], and the Na_2O from this second reaction be soluble. Then the material can be recycled, and the only effect would be a recirculating sodium load in the solid circuit. If, on the other hand, the insoluble compound was inert to further reaction, active sodium and metal oxide would be removed from the process streams. Inert would accumulate and would have to be purged. In this case a workable process would not be obtained.

STOICHIOMETRY

The overall reaction was expressed in Eq. (4) as,

$$Na_2CO_3 + nM_xO_y = Na_2O\cdot(M_xO_y)_n + CO_2$$

However, the stoichiometry is not as straightforward as it appears in this expression. The stoichiometric coefficient, n, is not necessarily an integer, and the value may change as the degree of conversion of Na_2CO_3 increases. The reason for this is that a number of the potential agents are polyacids (e.g., SiO_3^{2-}, BO_2^-, TiO_3^{2-}, and PO_3^-). The characteristic feature of the polyacids is the linking of single groups by means of oxygen bridges. For example $[BO_2^-]_n$ may consist of BO_3 groups linked together to form chains



or rings where each BO_3 group shares two oxygen atoms (20). As a consequence, the transition of a polyacid to its corresponding base requires the breaking of an oxygen bridge with a simultaneous binding of an oxygen atom. These reactions may be considered to consist of an acid-base reaction (the transition of an oxygen ion from one degree of polarization to another) and a polymerization reaction (21):

1. acid-base reaction

$$BO_3^{3-} = \frac{1}{2}(BO_{2.5}^{2-})_2 + \frac{1}{2}O^{2-} = (1/n)(BO_2^-)_n + O^{2-} \qquad (20)$$

2. polymerization

$(BO_2^-)_3$ (ring with three links)

$(BO_2^-)_4$ (ring with four links)

etc.

As a result of these factors, there is no definite proportion between the oxide and the carbonate. For example, in the borate system one can have

$$Na_2CO_3 + 1/2\ B_2O_3 = 1/2\ Na_4B_2O_5 + CO_2 \qquad (21)$$

$$Na_2CO_3 + B_2O_3 = 2NaBO_2 + CO_2 \qquad (22)$$

$$Na_2CO_3 + 2B_2O_3 = Na_2B_4O_7 + CO_2 \qquad (23)$$

Another consequence is that some of the salts themselves can act as decarbonizing agents

$$Na_2B_4O_7 + Na_2CO_3 = 4NaBO_2 + CO_2 \qquad (24)$$

and

$$2NaBO_2 + Na_2CO_3 = Na_4B_2O_5 + CO_2 \qquad (25)$$

The actual relationship that will exist will depend on the equilibria of a number of sequential and parallel reactions, and thus will be dependent on the temperature and CO_2 concentration in the gas phase. Interpretation of data requires relating extent of conversion of Na_2CO_3 to the molar ratio of metal oxide and sodium at different temperatures and CO_2 concentration.

Equilibria

It is highly likely that chemical equilibria restraints will have a significant influence on smelt decarbonization. It was postulated earlier that the reaction could be considered as involving two distinct steps:

$$CO_3^{2-} = O^{2-} + CO_2(g) \quad (11)$$

and

$$M_xO_y + O^{2-} = M_xO_{y+1}^{2-} \quad (12)$$

Either or both of these reactions can be reversible. It was just mentioned that the metal oxides can be acting as polyacids, and that the complex equilibria among the various degrees of polymerization can complicate the stoichiometry. However, the most important equilibrium from a commercial standpoint is likely to be that of reaction 11 and its dependence on CO_2 concentration.

If both reactions (11) and (12) are at equilibrium and all components are molten (or soluble), the equilibrium would be given by

$$[CO_3^{2-}] = \frac{K_{11}}{K_{12}} \left[\frac{M_xO_{y+1}^{2-}}{M_xO_y} \right] P_{CO_2}$$

This suggests that the final carbonate concentration (and hence degree of decarbonization) will be directly proportional to the concentration of CO_2 in the surrounding atmosphere. It also suggests that the reaction can be driven to completion by removal of CO_2 from the system.

The commercial application of smelt decarbonization in a recovery furnace would take place in an atmosphere containing a significant concentration of CO_2. Thus relevant data would be those taken at P_{CO_2} levels of about 0.1 to 0.2 atmosphere. Very little systematic information has been published on the equilibria of these reactions. The limited data that are available will be included in the discussion of specific decarbonizing agents.

Reaction Kinetics

Smelt decarbonization involves the reaction of molten Na_2CO_3 with either a solid or liquid decarbonizing agent. If both components are liquid, the reaction is

homogeneous. Rate equations for the homogeneous case for a number of different assumptions about the rate limiting step are derived in Appendix I. These indicate that the reaction rate could be 1st, 2nd or 3rd order in carbonate concentration, and inversely proportional to some power of CO_2 concentration.

When the decarbonizing agent is a solid at reaction conditions, the reaction would be heterogeneous. The concentration of M_xO_y would not enter into the rate equation, but its surface area would. The rate equation could involve diffusion terms and the overall rate of conversion would likely be slower than for the homogeneous reaction. Reaction (11) (carbonate decomposition) might be in equilibrium in the bulk phase with O^{2-} diffusing to the reaction surface. In addition, the surface area of the M_xO_y would change in an unpredictable manner as the reaction proceeds. No general kinetic expression can be written for this heterogeneous case.

CHEMISTRY OF AUTOCAUSTICIZING SYSTEMS

The emphasis of this section is on those aspects of the chemistry of these systems which bear on pulping and recovery operations. The discussion is based mainly on the work of Janson (7-9). Most of his work was with boron compounds because they showed the most promise as pulping chemicals.

BORATES

There are a number of different decarbonization reactions possible with B_2O_3 (see reactions 21-23). The products and some important system characteristics are summarized below.

Product	Na:B	Solution pH
$Na_4B_2O_5$	2	13.5-14
$NaBO_2$	1	11-12
$Na_2B_4O_7$	1/2	9

It is evident that only $Na_4B_2O_5$ is alkaline enough to be used as a pulping reagent. This means that the Na:B molar ratio in the system must be at least 2. There is no advantage to operating at higher ratios than this since $Na_4B_2O_5$ is not an effective decarbonizing agent. That is, the reaction

$$Na_4B_2O_5 + Na_2CO_3 \rightarrow 2Na_3BO_3 + CO_2 \qquad (27)$$

does not go.

Stoichiometry

Since an ideal borate autocausticizing system operates at a Na:B ratio of 2 and involves water soluble salts circulating around the system, the smelt decarbonizing reaction can be considered to be

$$2NaBO_2 + Na_2CO_3 = Na_4B_2O_5 + CO_2 \quad (25)$$

When the ratio of Na:B in the system is less than 2, the reaction

$$Na_2B_4O_7 + Na_2CO_3 = 4NaBO_2 + CO_2 \quad (24)$$

could also be involved.

When $Na_4B_2O_5$ is dissolved in water it becomes

$$Na_4B_2O_5 + H_2O \rightarrow 2NaOH + 2NaBO_2 \quad (28)$$

and

$$2NaBO_2 + 4H_2O \rightarrow 2NaB(OH)_4 \quad (29)$$

The part of the $Na_4B_2O_5$ which is active for pulping is the NaOH equivalent, while the $NaB(OH)_4$ (or $NaBO_2$ in anhydrous form) is inert for pulping.

The chemistry of the entire cycle can then be summarized as follows:

$$Na_2CO_3 + 2NaBO_2 \rightarrow Na_4B_2O_5 + CO_2 \quad \text{(decarbonizing)}$$

$$Na_4B_2O_5 + H_2O \rightarrow 2NaOH + 2NaBO_2 \quad \text{(caustic forming)}$$

$$NaBO_2 + 2H_2O \rightarrow NaB(OH)_4 \quad \text{(hydration)}$$

$$NaOH + \text{Org H} \rightarrow \text{Org Na} + H_2O \quad \text{(pulping)}$$

$$NaB(OH)_4 \rightarrow NaBO_2 + 2H_2O \quad \text{(dehydration)}$$

$$\text{Org Na} \rightarrow Na_2CO_3 \quad \text{(combustion)}$$

It can be seen that there is essentially a constant load of $NaBO_2$ present throughout the system. In a closed pulping and recovery system, the only boron compounds added would be a small amount of make-up to maintain the Na:B ratio at the desired value (close to 2).

Degree of Conversion

Janson (7,8) investigated how the extent of decarbonization depended on the molar Na:B ratio, temperature and CO_2 concentration. He carried out a series of reactions at 875°C in a N_2 atmosphere in which the Na:B ratio was varied at constant borate and carbonate charge. This was achieved by adding various amounts of NaOH to a fixed amount of Na_2CO_3 and H_3BO_3 prior to heating up the charge. He found CO_2 was completely eliminated from a borate/carbonate smelt for Na:B < 1.5. CO_2 elimination was 80-90% at Na:B = 2.0 and decreased linearly to about 10% at Na:B = 3.0. Above Na:B = 3.5, no CO_2 was expelled. These results need interpretation. Complete decarbonizing for Na:B $\leq$ 1.5 is a reflection of the fact that $Na_2B_4O_7$ is a more effective decarbonizing agent than $NaBO_2$ because it is more acidic. As the Na:B ratio approaches 2 the borate is present as $NaBO_2$. The fact that the conversion was only 80-90% may be a kinetic phenomenon, since both $NaBO_2$ and Na_2CO_3 would be nearly depleted as conversion approaches 100%. At higher Na:B ratios more of the borate is present as $Na_4B_2O_5$ which is too alkaline to serve as a decarbonizing agent. The relative proportion of $NaBO_2$ and $Na_4B_2O_5$ will shift linearly between Na:B = 2 and Na:B = 3, and the CO_2 release decreases in a like manner. Thus all Janson really showed was that $Na_2B_4O_7$ was a better decarbonizing agent than $NaBO_2$, and that $Na_4B_2O_5$ was ineffective.

Since a commercial borate based alkaline pulping system would in effect operate with a continuously circulating load of $NaBO_2$, the relevant question is how does the conversion change with Na:B ratio when the reactants are $NaBO_2$ and Na_2CO_3 and a change in Na:B ratio represents a change in the relative proportion of these two reactants. Janson did not obtain this type of data. His most significant point is the 85% conversion at Na:B = 2, which is probably a kinetic phenomenon. At higher values of Na:B, the conversion of Na_2CO_3 would be limited by the amount of

$NaBO_2$ present. However, the concentration of Na_2CO_3 would be higher through the course of the decarbonization, so kinetic limitations might be less. Thus a gradual decline in Na_2CO_3 conversion might be expected from the 85% at Na:B = 2 to the stoichiometric limit of 50% at Na:B = 3.

Experiments at 1150°C gave complete elimination of CO_2 at all initial Na:B ratios tested. However, both Na and B were volatized at these higher temperatures, and the final Na:B ratio never exceeded 1.5. Thus these results were inconclusive.

The extent of conversion of Na_2CO_3 was significantly reduced when a CO_2 atmosphere was present. Janson (8) obtained his data by two different techniques: batch tests in crucibles in a muffle furnace with 10 g samples, and TGA (thermogravimetric analyses) using 10 mg samples. The results are shown in Table II. Both techniques showed substantially lower CO_2 elimination under a CO_2 partial pressure of 18-19%. The two methods gave somewhat inconsistent results in that the TGA method always gave higher conversions at a given temperature. This result may have been due to more effective reabsorption of CO_2 in the larger samples (Janson's explanation) or an increased volatilization of Na and B from the smaller TGA samples.

Similar autocausticizing experiments in the presence of Na_2S showed that Na_2S had no effect on the autocausticizing reactions.

The main conclusion from Janson's data is that the presence of CO_2 in the surrounding atmosphere does retard carbonate decomposition in borate-autocausticized smelts. The effect is quite marked at temperatures below 1000°C, but becomes less at higher temperatures. His data are inconclusive as to whether this is solely a kinetic effect or a consequence of an equilibrium limit, although the general

behavior suggests an equilibrium. There is a definite need for precise data on equilibria in closed systems where volatility of inorganics does not obscure results.

TABLE II

AUTOCAUSTICIZING CONVERSION VERSUS TEMPERATURE

(Na:B Molar Ratio = 2)

	Percent of Initial CO_2 Released[a]			
	TGA		Crucible	
Temperature, °C	N_2	18% CO_2	N_2	18% CO_2
600	19	8	0	0
750	92	8	77	31
950	116	86	96	52
1050	121	> 124	98	81

[a] CO_2 release for TGA experiments as $\frac{\text{weight loss}}{\text{initial } CO_2} \times 100$

crucible samples were analyzed for residual CO_3^{2-}.

Reaction Kinetics

Janson (8) found very different conversion rates depending on the technique employed. Experiments with 10 g samples in a crucible in a muffle furnace gave a generally slow reaction, requiring 3.5 hours to be completed at 875°C. Experiments using 10 mg samples on a TGA microbalance went to completion in 10 minutes at 700°C. The latter, as mentioned previously, involved considerable volatization of Na and B and the final Na:B ratio approached 1.5:1, where CO_2 release would tend to be more rapid.

The interpretation of kinetic data must be done carefully. The decarbonization reactions would be expected to be endothermic (heat absorbing), and to have reasonably high activation energies (reaction rate increases significantly as temperature is increased). Whenever reactions having these characteristics are

carried out in batch mode, the overall reaction kinetics can tend to be heat transfer controlled. In addition, where a reaction product (such as CO_2) can react to reverse the reaction, the mass transfer of that product out of the reacting mass can control the overall reaction rate.

Applying these concepts to Jansons work, it is likely that the crucible experimental results were heavily influenced by heat and mass transfer effects, while the TGA runs were not. However, the TGA experiments were done on a very open system and the stoichiometry shifted in an uncontrolled manner to a region which is not of practical interest. For this reason the results obtained on the TGA system are not considered reliable.

The kinetic data that Janson obtained could be fit to either a 2nd or 3rd order reaction model with respect to carbonate concentration. The data are not precise enough to distinguish between 2nd or 3rd order. The implications of reaction order with respect to rate controlling steps is given in Appendix I.

Janson fit his data to a second order rate equation,

$$\frac{1}{(CO_3^{2-})} - \frac{1}{(CO_3^{2-})_0} = kt \qquad (30)$$

with

$$\ln K = 20.11 - 43{,}100/RT \qquad (31)$$

where (CO_3^{2-}) = mole fraction Na_2CO_3 in smelt

$(CO_3^{2-})_0$ = initial mole fraction of Na_2CO_3

t = time, hours

K = rate constant, $(\text{hour} \cdot \text{mole fraction})^{-1}$

R = gas constant, 1.987 cal/mol °K

T = temperature, °K

The activation energy, of 43,100 cal/mole indicates that reaction rates are quite sensitive to temperature.

Other Considerations

The presence of borates in molten carbonate reduces the loss of sodium from the smelt. Janson's data show that appreciable volatilization of Na in a reducing atmosphere began around 700°C for carbonate smelts. Borate-carbonate smelts (Na:B = 2) did not begin to lose Na until about 900°C. Borate was not volatilized below 1050°C. Both a CO_2 atmosphere and Na_2S in the smelt increased the temperature at which substantial Na volatilization began by about 50°C.

Sodium borates lower the melting point of smelts. Ten mole percent is reported to lower the melting point of pure Na_2CO_3 by 280°C, and a patent has been issued for using borates for improving smelt fluidity in soda pulping and recovery (22). However, the smelt becomes glassy on cooling and is not as easy to dissolve as smelts without borate.

Dead Load

There is a substantial dead load in borate autocausticizing systems because of the $NaBO_2$ needed to have the decarbonizing reaction go. As discussed earlier [Eq. (18)] the dead load is give by

$$\frac{(1-C) + S}{0.755\ C}$$

where C is the fractional conversion of Na_2CO_3 and S is the weight ratio of the decarbonizing agent ($NaBO_2$) to Na_2CO_3 before decarbonizing. This weight ratio, S, can be related to the molar Na:B ratio in the system by,

$$S = \frac{65.8}{53(r-1)} \qquad (32)$$

where r = molar Na:B ratio.

Then the dead load is given by

$$\text{Dead Load} = \frac{(1-C) + \frac{65.8}{53(r-1)}}{0.755\ C}, \text{ lb/lb NaOH} \qquad (33)$$

Using Janson's data on conversions (C) for r values up to 2, and a linear relation between C = 0.85 at r = 2 and C = 0.5 at r = 3, the data in Table III were obtained.

TABLE III

DEAD LOAD IN BORATE SYSTEMS

Na:B ratio	1.5	1.8	2	2.2	2.5	3.0
% Conversion:	100	92	85	78	67.5	50
Dead Load lb/lb NaOH:	3.29	2.35	2.17	2.13	2.26	2.97

The desirability of operating at an Na:B ratio of 2 or slightly greater is evident. At lower values too much $NaBO_2$ is present and at higher values, too much unreacted Na_2CO_3. However, even at the minimum point, the recirculating dead load is 6-7 times that which would be normally encountered in conventional causticizing. In addition, the conversion values used in the above Table were based on Janson's values for a N_2 atmosphere. Conversions were significantly lower when CO_2 was present, and this would lead to even higher dead loads.

OTHER AUTOCAUSTICIZING AGENTS

Phosphates

Phosphates can also be used as smelt decarbonizing agents. The reaction which is involved is

$$\underset{\text{(pyrophosphate)}}{Na_4P_2O_7} + Na_2CO_3 \rightarrow \underset{\text{(orthophosphate)}}{2Na_3PO_4} + CO_2 \qquad (34)$$

The chemistry which would be involved in an alkaline pulping cycle based on phosphates is

$$\underset{(pH\ \ 13)}{Na_3PO_4} + Org\ H \rightarrow Org\ Na + Na + \underset{(pH\ \ 10)}{Na_2HPO_4} \qquad (35)$$

$$2Na_2HPO_4 \rightarrow H_2O + Na_4P_2O_7 \qquad (36)$$

and reaction (34) above. This is not quite alkaline enough to be suitable for pulping, and phosphate systems are not very attractive for this reason. Janson has suggested that they could be used for alkali-oxygen pulping.

Pyrophosphate is a more effective decarbonizing agent than $NaBO_2$. Janson found the rate of decarbonization was much more rapid, going to completion in less than 30 minutes in the temperature range 625-875°C. Decarbonization went to completion for Na:P ratios of 3 or less in agreement with reaction (34).

In contrast to the borate results, decarbonization with pyrophosphate was only slightly inhibited by a CO_2 back pressure. This parallels the other evidence that pyrophosphate is a more effective decarbonizing agent than borate. This is basically due to pyrophosphate being somewhat more acidic, and is not unrelated to the fact that phosphate autocausticizing products are not alkaline enough to be suitable pulping agents.

The cooled product after decarbonizing formed a porous powder easy to dissolve in water, in contrast to the glassy, slowly dissolving borates. However, this may mean that the material from phosphate autocausticizing would not flow from the furnace as a smelt, and that kilns or fluidized beds would be needed for combustion in phosphate autocausticizing systems.

Silicates

Sodium silicate, Na_2SiO_3, gives quite strongly alkaline solutions (pH > 13) and can be formed by a smelt decarbonizing reaction,

$$Na_2Si_2O_5 + Na_2CO_3 \rightarrow 2Na_2SiO_3 + CO_2 \quad (37)$$

The Na_2SiO_3 would be converted back to $Na_2Si_2O_5$ during pulping in a manner directly analogous to that for borates or phosphates.

The decarbonization reaction with silicates is somewhat more sluggish than in the case with borates, although it goes in about the same temperature range. The presence of a CO_2 atmosphere retarded carbonate conversion slightly, but less than in the borate systems. An Na:Si ratio of 2 or less was required for complete CO_2 elimination. The cooled smelt becomes glassy and was difficult to dissolve.

The solution chemistry of silicates is very complicated. Experience with the alkaline pulping of materials containing large amounts of silica has shown that soluble silicates are extremely likely to form glassy scales on evaporator surfaces. The combustion of these liquors has also proved to be troublesome. Thus it is very unlikely that a silicate based autocausticizing system would be attractive.

Aluminates

The decarbonizing reaction may be represented by:

$$Al_2O_3 + 2\ Na_2CO_3 \rightarrow Na_4Al_2O_5 + 2\ CO_2 \quad (38)$$

This is a heterogeneous reaction since Al_2O_3 is a solid in the temperature region of interest. Decarbonization was much more sluggish than for any of the other agents, requiring a higher temperature, (1150°C as opposed to 875°C). Although Eq. (38) indicates that a Na:Al ratio of 2 to 1 should be sufficient for complete CO_2 release, experiments showed a ratio $\leq$ 1.5 was needed to drive the reaction to completion. The effect of a CO_2 atmosphere on conversion was not studied.

Aluminate systems do not appear to be at all attractive for alkaline pulping. Insoluble aluminum compounds are likely to precipitate out at a number of steps in the process. This could lead to scaling problems, precipitation on pulp and other problems.

SUMMARY

The following statements summarize the results of this review of the chemistry of autocausticizing systems.

1. Borate systems are the only viable autocausticizing systems for commercial alkaline pulping. Phosphate systems are too weakly alkaline. Silicate and aluminate systems have marginal alkalinity and would be very prone to precipitation problems during pulping and recovery.

2. A borate autocausticizing system would operate with a steady-state inventory of borate in the system at a molar ratio Na:B of 2 or slightly greater. The actual agent serving to decarbonize smelt would be $NaBO_2$.

3. There would be a significant dead load of inorganic salts ($NaBO_2$ and Na_2CO_3) in the pulping and recovery system. The magnitude is shown in Fig. 1. The dead load for conventional causticizing is also shown.

4. The conversion of Na_2CO_3 by borate is inhibited by the presence of CO_2 in the surrounding atmosphere. Reliable data on these effects are not presently available. There is a need for a quantitative definition of the equilibria for the borate decarbonizing reaction.

5. The kinetic data available may be sufficient to estimate conversion rates in the furnace if the conversion rates are limited by the

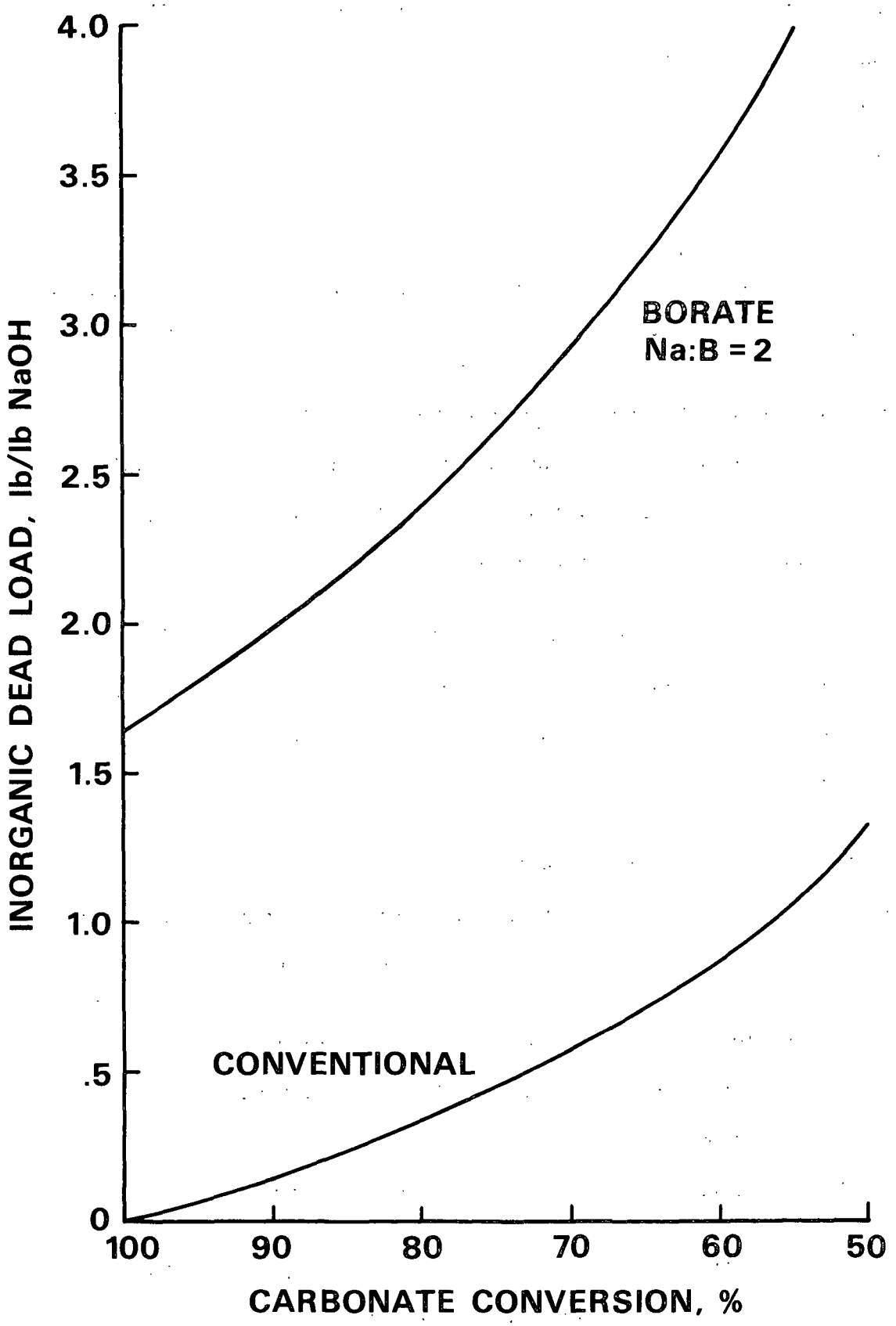


Figure 1. Dead Load Chemicals in Borate Autocausticizing System

chemical reaction itself. However, decarbonization in a recovery furnace may be heat transfer limited.

CHEMISTRY OF SMELT CAUSTICIZING SYSTEMS

This section is concerned with the chemistry of those smelt decarbonization systems in which the reaction product is not soluble and therefore the decarbonizing agent does not recirculate around the system. It is based mainly on the work of Kiiskila et al. (1,2,10-13) and the patent of Nagano et al. (15). The emphasis is on those aspects of the chemistry which bear on pulping and recovery operations.

TiO_2 SYSTEMS

The stoichiometry of decarbonizing with TiO_2 can be written as

$$a\ Na_2CO_3 + b\ TiO_2 = a\ Na_2O{\cdot}b\ TiO_2 + a\ CO_2 \qquad (39)$$

where a:b can be 1:6, 1:3, 1:2, 4:5, 1:1 or 2:1. In a commercial system it would be desirable to minimize the amount of expensive TiO_2 required so the main interest is in the reaction with high ratios of Na_2O:TiO_2. Kiiskila found that these reactions proceed in either the solid or molten phase, but are much faster with molten Na_2CO_3. The reactions proceed sequentially from low ratios of Na_2O:TiO_2. The reaction with a:b = 4:5 goes at lower temperature (850-950°C) but converts to a 1:1 ratio at higher temperatures. Spontaneous decomposition and Na_2O loss becomes significant above 1000°C.

The hydrolyis react on with TiO_2 is not totally straightforward. Ideally, this reaction would be written

$$a\ Na_2O{\cdot}b\ TiO_2 + a\ H_2O \rightarrow 2a\ NaOH + b\ TiO_{2(s)} \qquad (40)$$

However, the hydrolysis reaction does not go to completion because sodium tritita-nate ($Na_2Ti_3O_7$ or $Na_2O{\cdot}3TiO_2$) is insoluble in water. Thus, in a commercial system operating at high ratios of Na_2O:TiO_2 (e.g., about 1 = 1), the hydrolysis reaction would actually stop at $Na_2Ti_3O_7$, i.e.,

$$a\ Na_2O \cdot b\ TiO_2 + (a - \frac{b}{3})H_2O \rightarrow \frac{b}{3}\ Na_2Ti_3O_7 + 2(a - \frac{b}{3})\ NaOH \qquad (41)$$

Since $Na_2Ti_3O_7$ is an effective decarbonizing agent,

$$Na_2Ti_3O_7 + 2Na_2CO_3 \rightarrow 3Na_2O \cdot TiO_2 + 2CO_2 \qquad (42)$$

the incomplete hydrolysis is not a major problem. The recycled agent would be $Na_2Ti_3O_7$ instead of TiO_2, and the net effect would be a recirculating Na load in the solids cycle at a Na_2O:TiO_2 ratio of about 0.33:1.

Degree of Conversion

Kiiskila found that reaction (39) went to completion in a CO_2-free atmosphere for Na_2O:TiO_2 ratios $\leq$ 1.0 in the temperature range 850-950°C. He found that the amount of decomposed Na_2CO_3 could be increased up to 1.5 moles Na_2CO_3/mole TiO_2 by increasing the temperature to 1100°C. The ratio of Na_2CO_3 converted per mole TiO_2 consumed was a strong function of temperature and only a weak function of initial Na_2O:TiO_2 ratio at high initial ratios. Apparently the sodium titanates are able to stabilize the Na_2O formed by Na_2CO_3 decomposition and prevent its volatization. However, this behavior was only observed in experiments with a CO_2-free atmosphere. Experiments carried out with a CO_2 partial pressure of 0.2 atmosphere did not yield more than 1 mole of Na_2CO_3 converted per mole of TiO_2 reacted. Relatively little data was presented for conversions in CO_2 atmospheres, but apparently conversion to $Na_2O \cdot TiO_2$ is not equilibrium blocked.

Reaction Kinetics

Kiiskila's kinetic data, obtained from crucible experiments are summarized in Table IV. These data show the fractional decomposition of Na_2CO_3 as a function of time at different temperatures and initial Na_2CO_3:TiO_2 ratios. These data were determined from weight loss assuming the weight loss was only due to escape of CO_2. All of these data were obtained for CO_2-free atmospheres. No kinetic data for CO_2-containing atmospheres were presented.

TABLE IV

FRACTION OF Na_2CO_3 DECOMPOSED AS A FUNCTION OF TIME AND TEMPERATURE IN THE SYSTEM Na_2CO_3 - TiO_2

x_0 = Initial Molar Ratio Na_2CO_3:TiO_2 [source: ref. (11)]

T, °C	t, min	x_0 = 0.189, x_1	x_0 = 0.503, x_1	x_0 = 0.755, x_1	x_0 = 1.000, x_1	x_0 = 1.132, x_1	x_0 = 1.500, x_1	x_0 = 1.761, x_1	x_0 = 2.000, x_1	x_0 = 3.019, x_1
850	5	0.499	0.485	0.466		0.429		0.303		0.191
	10	0.777	0.647	0.604	—	0.568	—	0.389	—	0.224
	15	0.851	0.736	0.669	—	0.628	—	0.424	—	0.241
	30	0.944	0.826	0.730	—	0.695	—	0.476	—	0.284
	60	1.000	0.888	0.804	—	0.741	—	0.520	—	0.328
	90	—	0.937	0.847	—	0.767	—	0.560	—	0.362
	120	—	0.976	0.877	—	0.789	—	0.588	—	0.383
900	5	0.882	0.729	0.712	—	0.603	—	0.427	—	0.249
	10	0.977	0.816	0.787	—	0.671	—	0.484	—	0.297
	15	1.000	0.872	0.828	0.799	0.706	0.639	0.513	0.480	0.328
	30	—	0.946	0.909	0.858	0.763	0.715	0.575	0.560	0.369
	60	—	0.991	0.965	0.933	0.834	0.816	0.644	0.650	0.432
	90	—	1.000	0.992	—	0.851	—	0.689	—	0.477
	120	—	—	1.000	—	0.876	—	0.718	—	0.504
950	5	0.977	0.867	0.782	—	0.699	—	0.524	—	0.358
	10	1.000	0.938	0.877	—	0.769	—	0.603	—	0.393
	15	—	0.968	0.926	—	0.803	—	0.647	—	0.423
	30	—	1.000	0.985	—	0.884	—	0.706	—	0.477
	60	—	—	1.000	—	0.923	—	—	—	0.518
	90	—	—	—	—	0.978	—	—	—	0.546
	120	—	—	—	—	0.992	—	—	—	0.559
1000	5	1.000	1.000	0.997	—	0.834	—	0.608	—	0.379
	10	—	—	1.000	—	0.890	—	0.596	—	0.385
	15	—	—	—	0.981	0.929	0.724	0.653	0.675	0.443
	30	—	—	—	0.999	0.974	0.867	0.692	0.728	0.480
	60	—	—	—	1.000	0.992	0.906	0.751	0.784	0.518
	90	—	—	—	—	1.000	—	0.791	—	0.542
	120	—	—	—	—	—	—	0.815	—	0.563
1050	5	—	—	1.000	—	0.872	—	0.665	—	0.436
	10	—	—	—	—	0.938	—	0.713	—	0.489
	15	—	—	—	—	0.959	—	0.737	—	0.516
	30	—	—	—	—	0.994	—	0.792	—	0.562
	60	—	—	—	—	1.000	—	0.844	—	0.617
	90	—	—	—	—	—	—	0.871	—	0.652
	120	—	—	—	—	—	—	0.894	—	0.679
1100	5	—	—	—	—	0.947	—	0.719	—	0.438
	10	—	—	—	—	1.000	—	0.777	—	0.503
	15	—	—	—	1.000	—	0.924	0.809	0.662	0.530
	30	—	—	—	—	—	0.997	0.856	0.740	0.583
	60	—	—	—	—	—	1.000	0.907	—	0.643
	90	—	—	—	—	—	—	0.954	—	0.690
	120	—	—	—	—	—	—	0.986	—	0.738
1150	5	—	—	—	—	0.989	—	0.777	—	0.465
	10	—	—	—	—	1.000	—	0.843	—	0.512
	15	—	—	—	—	—	—	0.883	0.714	0.546
	30	—	—	—	—	—	—	—	0.724	0.605
	60	—	—	—	—	—	—	—	—	0.707
	90	—	—	—	—	—	—	—	—	0.823
	120	—	—	—	—	—	—	—	—	0.930
1200	5	—	—	—	—	—	—	0.784	—	0.518
	10	—	—	—	—	—	—	0.845	—	0.593
	15	—	—	—	—	—	—	0.887	0.800	0.646
	30	—	—	—	—	—	—	0.959	0.850	0.792

The data show that smelt decarbonization with TiO_2 is relatively rapid, going to completion in an hour at 950°C and 30 minutes at 1200°C. The general shape of the kinetic curves is an extremely rapid reaction rate initially, followed by a rather distinct break and a long period of much slower conversion. Kiiskila explained this as being due to rapid formation of $4Na_2O \cdot 5TiO_2$ and much slower conversion (under diffusion controlled conditions) to $Na_2O \cdot TiO_2$. No estimate of the activation energy for these reactions was made.

Hydrolysis

As mentioned previously, the hydrolysis reaction does not go to completion with TiO_2. About 1/3 mole Na_2O per mole TiO_2 remains undissociated. This is due to the formation of insoluble sodium trititanate ($Na_2Ti_3O_7$ or $Na_2O \cdot 3TiO_2$). Only the Na_2O bound in excess of this amount is hydrolyzable to form NaOH. The hydrolysis reaction reaches equilibrium in about 30 minutes and is insensitive to hydrolysis temperature in the range 60-100°C. The hydrolysis equilibrium is independent of NaOH concentration up to about 100 g/L. Above that, a smaller fraction of the Na_2O is converted to NaOH.

Kiiskila showed that the insoluble product from TiO_2-Na_2CO_3 reactions could be recycled and was active as a decarbonizing agent. He took the insoluble product and reacted it with fresh Na_2CO_3 at a fixed ratio of Na_2CO_3 to TiO_2, and repeated this for a number of cycles. The steady-state level of unhydrolyzable Na_2O was about 0.33 mole/mole TiO_2. After the first cycle, the NaOH yield depended only on the initial Na_2CO_3 to TiO_2 ratio. Since the initial cycle would involve some formation of $Na_2Ti_3O_7$ from TiO_2, and this requirement is automatically satisfied in the recycled TiO_2, these results show that the recycled solids ($Na_2Ti_3O_7$) are effective decarbonizing agents, and that the Na_2O formed from this reaction is essentially completely hydrolyzable. For Na_2CO_3/TiO_2 ratios below 1.0, the caustic (NaOH) yield is nearly 100% with recycled solids.

Thus the incomplete hydrolysis would have a minimal effect on the commercial utilization of TiO_2 smelt causticizing. The weight of recycled solids would increase slightly (about 25%) and there would be an inventory of sodium tied up. In addition, make-up TiO_2 would be less effective than recycled TiO_2 (actually trititanate) in forming caustic. Otherwise the system should be operable.

Stoichiometry

The system would operate with a $Na_2O:TiO_2$ molar ratio of about 1 to 1.3, depending on the degree that CO_2 concentrations affect conversion. Kiiskila's experiments with recycled solids indicated essentially complete conversion to NaOH. This could be represented by the following sets of reactions.

$$3Na_2CO_3 + Na_2Ti_3O_7 \rightarrow 4Na_2O\cdot 3TiO_2 + 3CO_2 \qquad (43)$$

and

$$4Na_2O\cdot 3TiO_2 + 3H_2O \rightarrow Na_2Ti_3O_7 + 6NaOH \qquad (44)$$

These results, which were obtained with a CO_2-free atmosphere, require 1.26 lb of recycled solids per lb NaOH formed.

If his results with a CO_2 partial pressure of 0.2 atm are relevant, then the limit to conversion is set by the product $Na_2O\cdot TiO_2$, and the reaction set is

$$2Na_2CO_3 + Na_2Ti_3O_7 \rightarrow 3(Na_2O\cdot TiO_2) + 2CO_2 \qquad (45)$$

and

$$3(Na_2O\cdot TiO_2) + 2H_2O \rightarrow Na_2Ti_3O_7 + 4NaOH \qquad (46)$$

Thus, if CO_2 inhibits conversion, the system would require 1.89 lb recycled solids/lb NaOH.

Fe_2O_3 SYSTEMS

Ferric oxide is an effective smelt decarbonization agent. The reaction can be written as

$$Na_2CO_3 + Fe_2O_3 \rightarrow 2NaFeO_2 + CO_2 \quad (47)$$

along with the corresponding hydrolysis reaction

$$2NaFeO_2 + H_2O \rightarrow Fe_2O_3 + 2NaOH \quad (48)$$

The use of ferric oxide as a smelt decarbonizing agent is limited to systems very low in sulfur content or sulfur-free systems because of the insoluble iron sulfides formed. Ferrous sulfide is sparingly soluble in water, and Fe_2S_3 decomposes to yield FeS and elemental sulfur when dissolved in hot water. In addition, the reducing atmosphere of a kraft furnace is sufficient to reduce Fe_2O_3 to FeO which is a less effective decarbonizing agent.

The reaction is not as simple as it appears in Eq. (47), since sodium ferrite and ferric oxide have a number of crystal forms and the actual reaction mechanism depends on temperature and the crystal forms involved. Kiiskila found that $\beta NaFeO_2$ is the more desirable form for the ferrite. He did not observe any alkali-richer mixed oxide compounds than $NaFeO_2$. Thus the minimum stoichiometric requirement for complete conversion of Na_2CO_3 is 1 mole Fe_2O_3/mole Na_2CO_3 as given in reaction (47).

Conversion

In a CO_2-free atmosphere, Na_2CO_3 is almost completely decomposed for initial molar Na_2CO_3:Fe_2O_3 ratios less than 0.5. Above a Na_2CO_3:Fe_2O_3 ratio of 1.5, the Fe_2O_3 is completely reacted, and the Na_2CO_3 conversion is stoichiometrically limited by the amount of Fe_2O_3 present. Between these values, ($0.5 < Na_2CO_3:Fe_2O_3 < 1.5$) the conversion of Na_2CO_3 drops almost linearly from 100% at 0.5 to the stoichiometric limit of 66.7% at 1.5 mole ratio.

The presence of a CO_2 atmosphere did not appreciably affect the conversion. TGA data showed about a 60°C increase in the temperature at which complete conversion was reached, while batch experiments in crucibles showed no difference in conversion at 900°C and 30 minutes reaction time.

Reaction Kinetics

Decarbonization with Fe_2O_3 is a relatively fast reaction. Kiiskila found that the reaction went to completion in less than 1 hour at 900°C or higher. Other workers (23,24) have reported it to be first order with respect to carbonate and to have an activation energy of 80-86 kJ/mole (19-20 kcal/mole).

Hydrolysis Reaction:

Kiiskila's data show that the reaction:

$$2NaFeO_2 + H_2O \rightleftarrows 2NaOH + Fe_2O_3 \qquad (48)$$

goes to 90% completion for $0.33 < Na_2CO_3/Fe_2O_3 < 1.5$. The combined conversion for smelt causticizing and hydrolysis yields a causticizing efficiency in the white liquor of greater than 85% when the initial mole ratio of Na_2CO_3/Fe_2O_3 is less than 1.0 and greater than 90% when the initial mole ratio is less than 0.67.

Nagano et al. (15) also reported causticizing efficiency data using soda black liquor and Fe_2O_3. Their data are compared with Kiiskila's in Table V. Although Nagano's data is based on an initial mole ratio of total liquor Na_2O/Fe_2O_3 instead of Na_2CO_3 and although the temperatures of the smelt decarbonization experiments were different, the causticizing efficiencies measured agree quite well.

Hydrolysis was quite rapid. At 95°C, the reaction was essentially completed in 15 minutes. The concentration of iron in the white liquor ranged from 0 to 2.2 ppm, with only 1.4 ppm Fe at a caustic concentration of 152 g NaOH/L.

TABLE V

EFFECTIVE CAUSTICIZING EFFICIENCY VS. INITIAL Na_2CO_3/Fe_2O_3 MOLE RATIO

	Kiiskila, et al. (12)	Nagano, et al. (15)
Smelt Decarbonizing Temperature, °C	1000	800
Initial Mole Ratio Na_2CO_3/Fe_2O_3:		
0.33	0.896	--
0.50	0.921	--
0.67	0.899	--
1.00	0.858	0.954
1.50	0.650	--
2.00	0.494	0.404
3.00	0.339	0.304

Stoichiometry

In order to ensure efficient decarbonization, it is necessary to use 1 to 1.25 moles of Fe_2O_3 per mole of Na_2CO_3. At an overall conversion of 90%, this results in a requirement of about 2.2 to 2.8 lb Fe_2O_3 per lb NaOH formed. The Fe_2O_3 that precipitates during hydrolysis can be recycled back and is effective as a decarbonizing agent. Thus there would be a recycle load back to the strong black liquor of about 2.2 to 2.8 lb Fe_2O_3 for every lb of NaOH in the white liquor.

ILMENITE SYSTEMS

Ilmenite consists mainly of iron(II) oxide and titanium dioxide, i.e., ($FeO \cdot TiO_2$). Its use as a smelt causticizing agent is as a potentially cheaper form of titanium oxide. Both components of ilmenite could become smelt decarbonizing agents if the ilmenite structure is broken and the FeO is oxidized to

Fe_2O_3. Because of the presence of iron, its use would be restricted to nonsulfur systems, similarly to the case with Fe_2O_3 alone.

It would appear that the basic chemistry of an ilmenite smelt-causticizing system would be as follows:

$$2\ FeO{\cdot}TiO_2 + 1/2\ O_2 \rightarrow Fe_2O_3 + 2\ TiO_2 \qquad (49)$$

and from then on the chemistry would be the same as for titanium dioxide or ferric oxide systems, namely;

initiation $\quad 3TiO_2 + Na_2CO_3 \rightarrow Na_2Ti_3O_7 + CO_2 \qquad (50)$

TiO_2 cycle

$$Na_2Ti_3O_7 + 2Na_2CO_3 \rightarrow 3(Na_2O{\cdot}TiO_2) + 2CO_2 \qquad (45)$$

$$3(Na_2O{\cdot}TiO_2) + 2H_2O \rightarrow Na_2Ti_3O_7 + 4NaOH \qquad (46)$$

Fe_2O_3 cycle

$$Na_2CO_3 + Fe_2O_3 \rightarrow 2NaFeO_2 + CO_2 \qquad (47)$$

$$2NaFeO_2 + H_2O \rightarrow Fe_2O_3 + 2NaOH \qquad (48)$$

In this view, ilmenite would only serve as an initial source of TiO_2 and Fe_2O_3 and as a means for supplying make-up to the system. The actual reactants circulating around the system would be $Na_2Ti_3O_7$ and Fe_2O_3 in the molar ratio of about 1.5 moles Fe_2O_3 per mole of $Na_2Ti_3O_7$. Then the key questions regarding the use of ilmenite are whether the decarbonizing and hydrolysis reactions of $Na_2Ti_3O_7$ and Fe_2O_3 are unaffected by the mutual presence of each other and whether the initial ilmenite will effectively yield $Na_2Ti_3O_7$ and Fe_2O_3 after a small number of passes through the system.

Kiiskila's data (13) are not completely conclusive on this point, but strongly suggest that a steady-state cycle, initiated by ilmenite, would essentially follow reactions 45-48 with a ratio of $Fe_2O_3/Na_2Ti_3O_7 = 1.5$ and with nearly

complete conversion at 1100°C. They also suggest the initial decomposition of ilmenite (first pass) is not as easy, since he got quite a bit of Na_2O loss by straight Na_2CO_3 decomposition in these runs.

SUMMARY

The following statements summarize the results of this review of the chemistry of smelt-causticizing systems.

1. Titanium dioxide systems are the only smelt causticizing systems operable in kraft recovery. Systems based on iron (ferric oxide) or mixed titanium-iron systems (ilmenite) are operable for nonsulfur alkaline recovery (soda, soda-AQ, oxygen-alkali) but not for kraft because of the formation of insoluble iron sulfides.

2. The actual smelt decarbonizing agent in a TiO_2 system operating at steady state would be sodium trititanate, $Na_2Ti_3O_7$. The amount of recycled solids ($Na_2Ti_3O_7$) would run about 1.9 lb solids/lb NaOH produced.

3. Dead load chemicals in the pulping and liquor concentration circuit would be no greater and (with high conversion efficiencies) could be substantially less than with present causticizing technology.

4. There do not appear to be any kinetic or equilibrium limits to carbonate conversion with either TiO_2 or Fe_2O_3 provided a sufficient amount of decarbonizing agent is used.

5. For sulfur-free systems, Fe_2O_3 may be the most attractive decarbonizing agent because of its lower cost. The amount of recycled solids (Fe_2O_3) would probably run about 2.5-2.8 lb solids/lb NaOH.

6. Ilmenite does not appear to be an attractive smelt-causticizing agent. It does not offer any particular advantages over either of its major components. It could be used only for sulfur-free systems because of the presence of iron, and in these ferric oxide is already quite suitable.

7. In conventional kraft technology, impurities which enter the system with the wood, make-up chemicals and water tend to be purged from the system at the green liquor clarifier. This purge operates because the impurities are insoluble in alkali. In a smelt-causticizing system, the impurities would precipitate along with the decarbonizing agent during hydrolysis. They would thus be recycled back to the heavy liquor and accumulate in the system. An alternative purge scheme would have to be developed.

8. There is a need for data on heats of reaction for smelt decarbonizing and hydrolysis. Data is also needed on the activation energies for the decarbonizing reactions in order to determine decarbonizing kinetics under possible heat transfer controlled conditions in the furnace.

APPLICATION TO KRAFT RECOVERY

The preceding review of the chemistry of various alternatives for autocausticizing and smelt causticizing highlighted some of the factors which would be important in commercial operation of such technologies and served to eliminate some from further consideration. In this section material and energy balances and preliminary cost analyses are developed for two of the approaches. These serve to focus attention on the advantages and disadvantages of these alternative technologies and to define the factors that are most critical to their technical and economic feasibility. Comparative balances and analyses are also presented for conventional kraft recovery to more clearly illuminate the differences between these technologies.

These analyses are limited to kraft recovery only, since this is by far the dominant alkaline pulping technology in use today. This restriction limits the number of alternatives which need to be considered in detail to two: autocausticizing with borate and smelt causticizing with titanates.

The procedure used is to develop comparative material and energy balances for conventional kraft recovery, borate autocausticizing and titanate smelt causticizing for a set of common conditions. These can then be used to define key advantages and shortcomings and provide a basis for economic assessments.

MATERIAL BALANCES

The following set of baseline conditions were defined for these material balances:

Pulp yield:	50%
Active alkali charge:	20%

Sulfidity:	30% (on active alkali)
Reduction efficiency:	90%
Chip moisture:	50%
Washing:	98% recovery at dilution factor = 2.5

There are differences in causticizing efficiencies and white liquor concentrations obtainable in these processes which influence the water balance and which must be considered. There are also potential changes in solubility limits which may influence results. Water balances over the digester neglected condensate from direct steaming and the evaporation loss during relief and blowing.

Conventional Process

The conventional process is assumed to operate at a causticizing efficiency of 80% and to produce a white liquor with a concentration of 6.4 lb/ft^3 A.A. (7.5 lb/ft^3 TTA) and a specific gravity of 1.15. The weak liquor is assumed to be concentrated in a multiple-effect evaporator to 50% solids and in a concentrator to 65% solids before being fired in the recovery boiler.

Borate Process

Janson's data on conversion with metaborates indicate that conversion of Na_2CO_3 may be significantly retarded by CO_2 atmosphere such as would exist in a recovery furnace. Accordingly two cases are considered for the borate process; conversion efficiencies of 80% and 60% with a Na:B ratio of 2.15 (excluding Na_2S and Na_2SO_4) in each. It is assumed that all Na_2CO_3 converted is hydrolyzed to NaOH, and that there are no limitations on white liquor concentration from borate solubility or hydrolysis equilibrium. The amount of water in the white liquor is governed by considerations in the digester and blow line. It was arbitrarily assumed that the dissolved solids concentration in the blow line should not exceed 25%. This was

taken to represent a value at which soap precipitation on the pulp could become a problem.

No information is available on the effects of very high levels of borate on the solubility of carbonate and sulfate in black liquor or on the solubility limits for the borate itself in black liquor. Lacking specific information it was assumed that the borate liquor with 80% conversion could be evaporated to 50% solids in the multiple-effect evaporators and 65% in a concentrator. Because of the high carbonate levels in the 60% conversion liquor, it was arbitrarily assumed evaporation was limited to 45% solids in the multiple effect evaporators and 63% out of the concentrator.

Titanate Process

It was assumed that this process operated with a conversion of 90% with a level of recycled $Na_2Ti_3O_7$ such that the $Na_2O:TiO_2$ ratio in the furnace (excluding Na_2S and Na_2SO_4) = 1. The hydrolysis of the converted Na_2CO_3 was assumed to be complete and the concentration of the white liquor produced was taken to be 7 lb A.A./ft^3 (101.3 g/L NaOH) with a specific gravity of 1.15. All $Na_2Ti_3O_7$ was assumed to be recycled, and the moisture of the recycled solids was taken to be 40%. Because of the very low amount of carbonate in the black liquor, it was assumed black liquor could be concentrated to 55% solids in the multiple-effect evaporators and 68% solids in the concentrator.

Results

The results of the material balance calculations are summarized in Table VI. The major differences between these processes show up at the recovery furnace. In all of the nonconventional processes the liquor solids to the furnace are

substantially higher than for the conventional process. Since the amount of dissolved organic is the same for all cases, the extra solids input reflects the much higher inorganic loads associated with smelt decarbonization. The water load to the furnace is likewise higher for the nonconventional cases. The effects of these two factors on the combustion of the black liquor will be discussed in greater detail in the energy balances section. Suffice it to say at this point that the higher inorganic and water loads per unit amount of organic could lead to combustion difficulties. In addition, the smelt flow for the nonconventional cases is from 50 to 100% greater than for the conventional. This could result in capacity limitations.

The importance of conversion efficiency for the borate process is clearly evident. The system with a conversion efficiency of 60% has such high inorganic loads as to be essentially unworkable. Since the laboratory studies were inconclusive as to the extent that CO_2 atmospheres inhibited conversion (yet did indicate that conversion could be a problem under furnace conditions) the need for further data on this point is evident.

A somewhat surprising feature of these data is that there is a rather small difference in the amount of water evaporated ahead of the furnace among the different processes. The evaporation loads ranged from 2.5% less than for conventional for titanate to 7% more than conventional for borate at 80% conversion. The only one really out of line was the borate case with 60% conversion, which again reflects the fact that high conversion efficiencies, $> 80\%$, are essential if autocausticizing or smelt causticizing are going to be commercially successful technologies. The main reason for the relatively small difference in evaporator loads is that other factors than equilibrium limits on white liquor concentration are important in the

overall water balance. The borate system balances take on the values they have because of the limitation of blow liquor solids content to 25%. If this is relaxed, the borate evaporation loads could be reduced. The moisture in the wood and the amount of wash water used contribute about half of the water in the weak black liquor, and this limits the impact of changes in white liquor concentration.

TABLE VI

ILLUSTRATIVE MATERIAL BALANCES
BASIS: 1 ADT PULP

	Conventional	Borate-I	Borate-II	Titanate
Carbonate Conversion, %	80	80	60	90
White liquor solids, lb	1,192	2,355	3,101	1,073
White liquor water, lb	6,880	8,430	10,660	6,310
Blow liquor solids, %	21.4	25	25	21.6
Weak black liquor, lb	17,770	20,460	23,420	17,080
WBL solids, lb	2,790	3,930	4,660	2,670
WBL solids content, %	15.7	19.2	19.9	15.6
Water evaporated in MEE, lb	12,190	12,600	13,060	12,230
Water evaporated in conc., lb	1,288	1,814	2,960	928
Water in heavy black liquor, lb	1,502	2,116	2,740	1,252
Recycled solids to furnace, lb	--	--	--	1,362
Water in recycled solids, lb	--	--	--	908
Total water to furnace, lb	1,502	2,116	2,740	2,160
Total solids to furnace, lb	2,790	3,930	4,660	4,032
Smelt out of furnace, lb	1,404	2,209	2,955	2,288
NaOH in white liquor, lb	650.3	650.3	650.3	650.3
Na_2S in white liquor, lb	271.7	271.7	271.7	271.7
Na_2CO_3 in white liquor, lb	215.4	215.4	574.5	95.7
Na_2SO_4 in white liquor, lb	55.0	55.0	55.0	55.0
$NaBO_2$ in white liquor, lb	--	1,162.7	1,549.5	--
$Na_2Ti_3O_7$ recycled, lb	--	--	--	1,362
Inorganic/organic at furnace	0.55	1.18	1.59	1.24
Water/organic at furnace	0.83	1.18	1.52	1.20

From an overall material balance standpoint, there is relatively little difference between the borate system at 80% conversion and the titanate system. In particular, the loads to the furnace are practically identical. The only adverse effect of having the soluble borate system (with the high dead load around the system) is about a 10% increase in evaporation requirements over the titanate

system. This would be counterbalanced by the need for a solids removal and return system for the titanate process which would not be needed for the borate process.

The key element involved in choosing between borate autocausticizing and titanate smelt-causticizing is then the impact on pulping. The titanate system produces a white liquor which is essentially no different from that produced conventionally, and thus there should be no impact on pulping. In the borate case, rather than pulping with a NaOH solution, the reagent is a borate solution of high alkalinity. The acid-base characteristics of the borate are then intimately involved in the pulping reactions. Hence the borate system might be expected to have some effect on pulping performance. That subject is not dealt with in this report.

ENERGY BALANCES

Three areas are considered in comparing the energy requirements for these different processes; evaporator steam demands, steam generation at the recovery boiler, and energy requirements in the remainder of the system. In addition, the likely impact on liquor combustion will be considered.

Evaporation

Steam is required for concentrating the liquors to the levels required for firing. The evaporation steam requirement can be estimated by using a steam economy of 4.5 lb H_2O evaporated/lb steam used for the multiple-effect evaporators and a steam economy of 1.7 for the concentrator. The steam requirement can be put on fuel Btu equivalent basis by assuming saturated steam at 35 psig and a steam generating efficiency of 85%. The results are shown in Table VII.

The impact of a low conversion efficiency in the borate system is clearly evident and this once again indicates the need for obtaining conversion efficiencies of at least 80%. Otherwise borate gives an evaporation energy demand about 10%

greater than the conventional. This is due mainly to an increase in concentration requirements above 50% solids due to the high dead load. Solubility limits would probably limit the solids levels obtainable in multiple effect LTV evaporators to no more than could be obtained with a conventional black liquor. Another effect which would be present in the borate system would be a much greater boiling point rise due to the high inorganic content. This would tend to lower the steam economy somewhat. However, it would be expected to have a greater effect on evaporator capacity.

TABLE VII

EVAPORATION ENERGY REQUIREMENTS
BASIS: 1 ADT PULP

	Conventional	Borate I	Borate II	Titanate
MEE steam demand, lb	2,710	2,800	2,900	2,720
Concentrator steam demand, lb	760	1,070	1,740	550
Fuel Btu equivalent, MM Btu	3.77	4.21	5.04	3.55
Δ Conventional, %	--	11.7	33.8	-5.8

The slight advantage that the titanate system shows is due mainly to the fact that the higher conversion efficiency (assumed 90%) reduces the amount of carbonate in the black liquor. Since carbonate-sulfate solubility tends to limit the solids concentrations obtainable in LTV evaporator, this effect was considered to allow achieving 55% solids in the MEE's at high steam economy with a corresponding reduction in the evaporation load at the lower efficiency concentrator.

Combustion

There are three main factors which need to be considered in analyzing liquor combustion in these processes. They are as follows:

1. Smelt decarbonization in the furnace will be an endothermic reaction and constitute an additional heat sink.

2. The high inorganic load will lower the heating value per lb of solids and will cause a greater heat removal with the inorganic products.

3. The extra water load will constitute an additional heat sink.

All of these factors will decrease the amount of steam generated per ADT pulp. They will also lower combustion temperatures and could lead to blackout problems.

The magnitude of the endotherm can be estimated from the following considerations (positive Δ H is endothermic and negative Δ H is exothermic).

Conventional:	$Na_2CO_3 + Ca(OH)_2 \rightarrow 2\ NaOH + CaCO_3$	$\Delta H = 0$
	$CaCO_3 \rightarrow CaO + CO_2$	$\Delta H = +\ 78{,}900$ Btu/mol
	$CaO + H_2O \rightarrow Ca(OH)_2$	$\Delta H = -\ 28{,}000$ Btu/mol
	$\therefore\ Na_2CO_3 + H_2O \rightarrow 2\ NaOH + CO_2$	$\Delta H = +\ 50{,}900$ Btu/mol
Borate:	$Na_2CO_3 + 2\ NaBO_2 \rightarrow Na_4B_2O_5 + CO_2$	$\Delta H = 50{,}900 + A$ Btu/mol
	$Na_4B_2O_5 + H_2O \rightarrow 2\ NaOH + 2\ NaBO_2$	$\Delta H = -A$ Btu/mol
	$\therefore\ Na_2CO_3 + H_2O \rightarrow 2\ NaOH + CO_2$	$\Delta H = +\ 50{,}900$ Btu/mol
Titanate:	$Na_2CO_3 + \frac{1}{2}\ Na_2Ti_3O_7 \rightarrow \frac{3}{2}\ (Na_2O \cdot TiO_2) + CO_2$	$\Delta H = 50{,}900 + B$ Btu/mol
	$\frac{3}{2}\ (Na_2O \cdot TiO_2) + H_2O \rightarrow 2\ NaOH + \frac{1}{2}\ Na_2Ti_3O_7$	$\Delta H = -B$ Btu/mol
	$\therefore\ Na_2CO_3 + H_2O \rightarrow 2\ NaOH + CO_2$	$\Delta H = 50{,}900$ Btu/mol

The fact that the net reaction is the same in all cases allows an estimation of the heats of reaction. The uncertainty is in how to apportion the heats of reaction between decarbonization and hydrolysis.

The heat of reaction for the borate decarbonization reaction, $Na_2CO_3 + 2NaBO_2 \rightarrow Na_4B_2O_5 + CO_2$ can be calculated from available thermodynamic data. Details are given in Appendix II. The value obtained is +66,610 Btu/mol Na_2CO_3. This means that the heat of the hydrolysis reaction, A, is -15,710 Btu/mol Na_2CO_3 converted.

This is substantially less than the heat released in slaking lime, and may well reflect the fact that the borate product is not as strongly alkaline as a pure NaOH solution.

Thermodynamic data on the titanate system are not readily available. Kiiskila did not report any thermal effects during dissolution of his titanate products, but he dissolved a relatively small amount of product in a relatively large quantity of water. Lacking more specific information, it will be assumed that the heat of the titanate hydrolysis is 1/2 that of lime, (i.e., B = 14,000 Btu/mol Na_2CO_3 converted) and the endotherm in the furnace would then be +64,900 Btu/mol or very close to that of borate.

A heat balance over the recovery boiler for each of the cases is given in Table VIII. The basis for the energy balance is 1 ADT. All of the heating value of the liquor is assumed to reside in the organic substances and the value chosen is 10,000 Btu/lb. This gives a heating value for the conventional liquor of 6,452 Btu/lb solids.

The balance is based on the heat loss method. Heat inputs include the heating value of the liquor and its sensible heat. The air is assumed to enter the unit at ambient conditions. Heat losses include the sensible heat in the dry flue gas, sensible and latent heat of water vapor, heat in smelt, heat of reduction, heat of decarbonization and radiation losses. Details of the calculation are given in Appendix III.

All of the nonconventional systems give less steam generation than does the conventional. For the borate system with reasonable conversion and the titanate system, the loss in steam generation is about 1.6 to 1.7 million Btu. The loss is about evenly divided between the heat of the decarbonizing reaction, the extra water

load, and the extra inorganic load. Of course, the process with low conversion efficiency gives even lower heat recovery.

TABLE VIII

RECOVERY BOILER ENERGY BALANCE
BASIS: 1 ADT PULP

(All Values in Millions of Btu's)

	Conventional	Borate I	Borate II	Titanate
Heating value black liquor	18.0	18.0	18.0	18.0
Sensible heat black liquor	0.51	0.71	0.87	0.73
Total input	18.51	18.71	18.87	18.73
Sensible heat dry flue gas	1.44	1.47	1.47	1.47
Heat in water vapor	2.96	3.70	4.45	3.75
Heat in smelt	0.81	1.28	1.71	1.33
Heat in reduction	1.20	1.20	1.20	1.20
Heat of decarbonization	--	0.54	0.54	0.53
Radiation	0.54	0.54	0.54	0.54
Total losses	6.95	8.73	9.91	8.82
Heat to steam (by difference)	11.56	9.98	8.96	9.91
Δ Conventional	--	-1.58	-2.6	-1.65
Specific heating value Btu/lb	6,452	4,580	3,863	4,464
Thermal efficiency, %	62.5	53.3	47.5	52.9

To a first approximation, the combustion temperature will tend to be proportional to the thermal efficiency since steam is basically obtained by cooling combustion gases. Using this criterion, combustion temperatures would be about 15% (or about 300°F) lower for both the borate and titanate systems. This could lead to

combustion instability and blackout problems. Increasing air temperature could help to alleviate this problem.

It should be noted that the expected reduction in combustion temperature is considerably less than the reduction in the specific heating value of the liquor solids (30%). The specific heating value can be a misleading criterion, since many of the effects of the low heating value can be overcome by increasing the solids throughput.

White Liquor Preparation

There are no significant steam demands in the white liquor preparation area for either of the nonconventional technologies. Equipment would be very simple in the borate system. The titanate system would need a filtration and transport system for the recycled $Na_2Ti_3O_7$, and also some means for purging impurities from the recycled solids. Energy requirements for this system are neglected in this balance.

The main energy requirement in the conventional process is the fossil fuel demand at the kiln, although the power requirements for the kiln drive and the pumps, filters, etc., are not necessarily negligible. The lime requirement in this case is calculated assuming stoichiometric lime addition and 80% conversion efficiency. This gives 570 lb CaO/ADT. Assuming 7 million Btu per ton of lime, the saving in fossil fuel at the lime kiln is 2.0 million Btu/ADT.

Digesters

There will be an increase in digester steam requirements for the borate system, because of the need to heat up the dead load salts and extra water to the cooking temperature. The digester incremental steam requirement can be assumed to be proportional to the total amount of white liquor charged. The heat requirement

can be estimated as that needed to bring the white liquor from 100°C to 170°C assuming a specific heat of 1 Btu/lb°F. The results are

Conventional	Borate I	Borate II	Titanate
0.865 MM Btu	1.155 MM Btu	1.474 MM Btu	0.791 MM Btu

By-product Power

A portion of the difference in energy requirements among these process alternatives is due to increased process steam demands. When the turbine capacity is available, the increased process steam demand represents an opportunity to generate by-product power at very high thermal efficiencies. This could partially offset the cost of the increased steam usage. This possibility has not been included in these particular balances.

Energy Balance Summary

The net increase and decrease in energy demand for the nonconventional processes is summarized in Table IX. All changes in steam demands are put on a fuel Btu equivalent basis by dividing by 0.85, since it is assumed that additional steam generation is by fossil fuel combustion at 85% thermal efficiency. The loss in steam generation at the recovery boiler is treated similarly.

Both of the nonconventional technologies show a reasonably good performance from an energy standpoint, as long as conversion efficiencies are high. The extra steam consumption and the loss in steam generation at the recovery boiler are just about counterbalanced by the savings in fuel for the lime kiln. Energy requirements do increase significantly as Na_2CO_3 conversion drops below about 80%.

TABLE IX

ENERGY REQUIREMENTS FOR NONCONVENTIONAL CAUSTICIZING
RELATIVE TO CONVENTIONAL PROCESS
BASIS: 1 ADT PULP

(All Values in Millions of Btu's)

	Borate I	Borate II	Titanate
Digester steam	0.29	0.61	-0.07
Evaporator steam	0.44	1.27	-0.22
Loss of steam generation at recovery boiler	1.86	3.06	1.94
Fuel for lime kiln	-2.00	-2.00	-2.00
Net change from conventional	0.59	2.94	-0.35

CHEMICAL MAKE-UP

There will be a certain amount of chemical losses from any one of these recovery technologies, which will require a certain amount of chemical make-up. The make-up chemicals likely to be used and their relative cost are listed below.

Conventional: Lime (CaO) @ 1.6¢/lb - 1.6¢/lb CaO

Borate: Borax decahydrate @ 8.5¢/lb - 9.4¢/lb $NaBO_2$

Titanate: TiO_2 (rutile) @ 35.5¢/lb - 28.2¢/lb $Na_2Ti_3O_7$
or sodium titanate @ 14-1/4¢/lb - 20.1¢/lb $Na_2Ti_3O_7$

It is evident that the decarbonizing agents are much more expensive per unit weight than is lime and this could lead to high chemical make-up costs for the nonconventional technologies.

For comparative purposes, we can assume a 10% per pass loss of lime for the conventional proces. With a total lime requirement of 570 lb CaO/ADT this gives 57 x 1.6 = $0.912/ADT for lime makeup for the conventional process.

Since borate is soluble in the system, its losses will correspond to other liquor losses. A washing efficiency of 98% was assumed in the material balances. This would lead to a make-up requirement of 23.25 lb $NaBO_2$ for the borate system at 80% conversion efficiency, or a cost of $2.19/ADT. With the relatively high cost of chemicals, more extensive washing to a higher recovery efficiency might be justified. On the other hand, washing losses are not the only source of chemical loss in a typical recovery system. Thus the assumed 2% loss may actually be conservative. For the borate make-up requirement to be no more costly than lime make-up would require a retention efficiency of 99.2% for the liquor solids. (For a conventional kraft mill this would amount to a total sodium make-up requirement of 16 lb salt cake per ADT).

The titanate situation is even worse. A loss of only 1% of the recirculating titanate would result in a make-up cost of $3.84/ADT if rutile is used and $2.74/ADT for sodium titanate make-up. The retention efficiency would have to be 99.67% to reach parity with lime make-up with the cheapest form of titanate make-up. Retention efficiencies of 98% are probably more realistic with make-up costs ranging from $5.50-$7.50/ADT.

Thus any operating cost advantages from reduced fuel usage for the nonconventional technologies is more than offset by the significantly higher costs for make-up chemical. Operating cost parity with the conventional process is only achievable with net chemical retention efficiencies which are significantly higher than is presently practiced.

CAPITAL REQUIREMENTS

It is not very straightforward to compare capital costs among the various alternatives. For a grass roots mill or one with a totally obsolete causticizing

and calcining system requiring complete replacement, the entire capital cost of the causticizing and calcining system is potentially a savings with the nonconventional processes. However, in most cases a functioning calcining and causticizing system is already present, (possibly overloaded) and the capital investment has already been made. In this situation there would be no savings in capital requirements unless the nonconventional technologies could be used to supply incremental capacity (giving a savings on the incremental capacity capital cost only). The latter situation would require coexistence of conventional and nonconventional causticizing in the same system. This does not appear favorable with borate, since the borate would be distributed throughout the entire pulping and recovery system. The NaOH formed by borate autocausticizing would inhibit Na_2CO_3 causticizing with lime. In addition, some borate would get into the lime mud and could interfere with calcination.

Coexisting causticizing would be possible with a titanate system provided that more than one recovery boiler was in use at the mill. In this case the titanate loop could be established over one recovery boiler while the remainder of the system would operate with conventional causticizing. The white liquors from the two processes would be combined just ahead of the digester.

The nonconventional causticizing processes are not free of capital requirements. Equipment needs for the titanate process include the following:

1. Modified dissolving tank to handle a precipitating solid, or means for handling and cooling smelt discharge for solid phase dissolution

2. Agitated holding tank(s) for hydrolysis reaction

3. White liquor clarifier

4. Titanate sludge washer and filter
5. Sludge conveyor and mixer for heavy black liquor
6. Auxiliary system for purging undesirable coprecipitants from recycled titanate.

The borate process has a minimum need for equipment in the white liquor preparation area (dissolving tank, white liquor clarifier-storage, and a dregs filter). However there are some hidden capital costs due to the adverse effect of the borate dead load on the capacity of other equipment around the pulping and recovery system. This is definitely a problem in the evaporators and possibly in the digester. The cost of the adverse effect on capacity could be borne by lost production, or by additional capital investment to restore the capacity to its original value.

Because of the complexities and uncertainties, no estimate of capital cost differences among the various alternatives has been made. There is likely to be some capital cost advantage for the nonconventional processes, but the advantage is likely to be less than 1/2 of the capital cost of a conventional causticizing-calcining process.

CONCLUSIONS

On balance, a comparison between conventional causticizing with lime and nonconventional causticizing technologies appears to favor the lime system. There do not appear to be any overwhelming advantages to the nonconventional processes and some of the drawbacks are potentially very serious.

Only two nonconventional processes appear feasible for kraft recovery, autocausticizing with borate and smelt causticizing with titanate. Ferric oxide is a suitable agent in nonsulfur systems, but is unsuitable for kraft because of the inevitable formation of insoluble iron sulfide. Other systems which have been discussed in the literature are not suitable for closed process recovery systems.

There is a marked increase in water and solids load to the recovery furnace in all of the nonconventional causticizing processes. This will significantly lower combustion temperature and could lead to combustion instability problems. This could result in a continuing need for auxiliary fuel to sustain combustion and could negate the advantage of eliminating the lime kiln fossil fuel requirement. The high solids and water load could also adversely affect recovery boiler capacity. In addition, smelt characteristics would be different and there could be difficulty in smelt drainage and dissolution.

A comparative energy balance showed relatively little difference between the conventional and nonconventional processes. The new technologies gave less steam generation from the recovery boiler and this was counterbalanced by the elimination of the need for fossil fuel at the lime kiln. Other differences tend to be minor.

Chemical make-up costs are significantly higher in the nonconventional systems because of the substantially higher unit cost of the chemicals employed.

This problem is more severe with titanate than with borate. Cost parity with conventional causticizing on make-up would require total recovery efficiencies significantly greater than those now obtained in practice. With reasonable values of recovery efficiencies excess make-up chemical costs could easily wipe out any other cost advantages of the nonconventional technologies.

The nonconventional technologies do have the potential for savings in capital costs compared with the conventional system. This is most significant in the case of a new mill and is less advantageous or even nonexistent in existing mills. The smelt causticizing system with titanate has a significant capital requirement itself and this reduces any comparative advantage with the conventional process. The borate autocausticizing system has little capital requirements per se, but will be prone to capacity reductions in the evaporators and other areas of the process.

In a choice between the nonconventional technologies, the economic advantage appears to be with the borate system. Make-up costs and capital costs are higher for the titanate system. However, the borate system requires that the alkaline borate solution be used directly in pulping. If this tends to slow the pulping rate or impair pulp quality, the advantage would shift to titanate.

There are some residual doubts about the technical feasibility of the borate process under commercial conditions. These have to do with the affect of CO_2 containing atmospheres on the conversion equilibrium. If a carbonate conversion efficiency of at least 80% cannot be maintained, the feasibility of the borate process rapidly diminishes.

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LITERATURE CITED

1. Kiiskila, E. and Virkola, N., Paperi Puu 3:129-32(1978).

2. Kiiskila, E., Paperi Puu 10:639-50(1979).

3. Janson, J., Paperi Puu (6-7):425-30(1977).

4. Janson, J. and Pekkala, O., Paperi Puu (9):546-57(1977).

5. Janson, J. and Pekkala, O., Paperi Puu (2):89-93(1978).

6. Janson, J., Paperi Puu (5):349-57(1978).

7. Janson, J., Paperi Puu (1):20-30(1979).

8. Janson, J., Paperi Puu (2):98-103(1979).

9. Janson, J., U.S. pat. 4,116,759(Sept. 26, 1978).

10. Kiiskila, E., Paperi Puu (5):394-401(1979).

11. Kiiskila, E., Paperi Puu (6-7):453-64(1979).

12. Kiiskila, E. and Valkonen, N., Paperi Puu (8):505-10(1979).

13. Kiiskila, E., Paperi Puu (9):564-77(1979).

14. Richter, G. A., U.S. pat 1,730,383(Oct. 8, 1929).

15. Nagano, T., Miyao, S., and Niimi, N., U.S. pat. 4,000,264(Dec. 28, 1976).

16. Lurie, R. J., U.S. pat 3,061,408(Oct. 30, 1962).

17. Cook, W. R., Tappi 57(9):94-6(Sept. 1974).

18. Sheeley, D. R., Rion, J. H., Cook, W. R., and Biggs, W. A., Jr., U.S. pat. 3,787,283(Jan. 22, 1974).

19. Sundheim, B. R. Fused salts. New York:McGraw-Hill Book Co., 1964. p. 50.

20. Flood, H., and Forland, T., Acta Chem. Scand. 1:592(1947).

21. Flood, H., Forland, T. and Roald, B., Acta Chem. Scand. (1):790-8(1947).

22. Fisher, W. E., U.S. pat. 3,873,413(March 25, 1975).

23. Frei, V., and Ceslavska, V., Chemiker-Ztg./Chem. Apparatus (89):399-402(1965).

24. Coates, A. W., and Redfern, J. P., Nature (201):68-9(1964).

25. Slough, W., and Jones, G. P. A compilation of thermodynamic data for borate systems. National Physical Laboratory Report Chem. 31, Aug. 1974.

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APPENDIX I

RATE EQUATIONS FOR BORATE AUTOCAUSTICIZING REACTIONS

For Na:B molar ratios between 1 and 2, the reaction mechanism could be described by the following equations.

$$B_2O_3 + O^{2-} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2\ BO_2^- \qquad (51)$$

$$CO_3^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} CO_2 + O^{2-} \qquad (52)$$

$$O^{2-} + 2\ BO_2^- \underset{k_6}{\overset{k_5}{\rightleftharpoons}} B_2O_5^{4-} \qquad (53)$$

Reactions (51) and (53) are a series/parallel pair following the carbonate dissociation step, reaction (52).

If reaction (52) is the rate determining step and (O^{2-}) is assumed to be near zero, the rate equation is

$$\frac{d(CO_3^{2-})}{dt} = -k_1\ (CO_3^{2-}) \qquad (54)$$

which is first order in carbonate concentration.

If reaction (51) is rate determining and irreversible:

$$\frac{d(CO_3^{2-})}{dt} = \frac{d(B_2O_3)}{dt} = -k_3\ (B_2O_3)\ (O^{2-}) \qquad (55)$$

(O^{2-}) is determined by the equilibrium of reaction (52) according to Eq. (56).

$$(O^{2-}) = \frac{k_1}{k_2}\frac{(CO_3^{2-})}{(CO_2)} \qquad (56)$$

If the initial concentrations of B_2O_3 and Na_2CO_3 are equal, then Eq. (55) becomes:

$$\frac{d(CO_3^{2-})}{dt} = -\frac{k_1k_3}{k_2}\frac{(CO_3^{2-})^2}{(CO_2)} \qquad (57)$$

which is second order in carbonate concentration and slowed as CO_2 partial pressure increases.

If reaction (53) is rate controlling and irreversible, and the initial concentrations of B_2O_3 (as $NaBO_2$) and Na_2CO_3 are equal, then $(B_2O_5^{4-}) = (CO_3^{2-})_0 - (CO_3^{2-})$.

$$\frac{d(B_2O_5^{4-})}{dt} = -\frac{d(CO_3)}{dt} = -k_5 (BO_2^-)^2 (O^{2-}) \qquad (58)$$

(BO_2^-) can be determined from the equilibrium relationships for Eq. (51):

$$(BO_2^-) = [\frac{k_3}{k_4} (CO_3^{2-}) (O^{2-})]^{1/2} \qquad (59)$$

and Eq. (57) becomes:

$$\frac{d(CO_3^{2-})}{dt} = -\frac{k_1 k_3 k_5}{k_2 k_4} \frac{(CO_3^{2-})^3}{(CO_2)^2} \qquad (60)$$

which is third order in carbonate concentration and also is slowed by increasing CO_2 partial pressure.

APPENDIX II

HEAT OF BORATE DECARBONIZATION

The borate decarbonization reaction is

$$Na_2CO_3 + 2NaBO_2 \rightarrow (2Na_2O)\cdot B_2O_3 + CO_2 \quad (61)$$

The heat of this reaction can be calculated from the sum of the reactions:

$$Na_2CO_3 \rightarrow Na_2O + CO_2 \quad (62)$$

$$2Na_2O + B_2O_3 \rightarrow (2Na_2O\cdot B_2O_3) \quad (63)$$

$$2NaBO_2 \; (= Na_2O\cdot B_2O_3) \rightarrow Na_2O + B_2O_3 \quad (64)$$

The heats for the general reaction,

$$a\ Na_2O + B_2O_3 \rightarrow a\ Na_2O\cdot B_2O_3 \quad (65)$$

are available in the literature for $0.25 \leq a \leq 1$ (25). These data were fit to the expression

$$-\Delta H_R = 262.15\ a^{0.701},\ KJ/mol \quad (66)$$

and used to obtain the value for $a = 2$ in Eq. (63).

The tabulated heats of reaction are then,

(62):	-178,590 - 169,283 - (- 484,997)	= + 137,124 Btu/lb mol
(63):	$-262.15 \times 2^{0.701} \times 429.9$ (Btu/lb mol/KJ/mol)	= -183,219 Btu/lb mol
(64):	$+ 262.15 \times 1^{0.701} \times 429.9$	= + 112,707 Btu/lb mol
(61):	Σ of the others	+ 66,612 Btu/lb mol

APPENDIX III

DETAILS OF RECOVERY BOILER HEAT BALANCE

All of the heating value in the black liquor was assumed to reside in the organic material with a heating value of 10,000 Btu/lb. The organic was assumed to consist of 56.6% carbon, 5.9% hydrogen and 37.5% oxygen. This was used to calculate stoichiometric air requirements and amounts of CO_2 and H_2O vapor produced by combustion. Twenty percent excess air was assumed.

Inorganic compounds were taken to be as given in the material balance (Table VIII in text). All of the NaOH in the white liquor was assumed present in the black liquor as if it were Na_2O. This was converted to Na_2CO_3 in the furnace in the conventional case, but exited as Na_2O in the borate and titanate cases.

Flue gas material balance data are summarized in Table X.

TABLE X

FLUE GAS CALCULATIONS
(BASIS: 1 ADT) PULP

	Conventional	Borate I	Borate II	Titanate
CO_2, lb	3,378	3,736	3,736	3,736
H_2O from combustion, lb	956	956	956	956
N_2 and O_2, lb	12,064	12,064	12,064	12,064
Total dry gas, lb	15,442	15,800	15,800	15,800
H_2O in liquor, lb	1,502	2,116	2,740	2,160
Total moisture in flue gas, lb	2,458	3,072	3,696	3,116

The heating value in the black liquor solids was the same in all cases, 1,800 lb organic x 10,000 Btu = 18,000,000 Btu. The sensible heat in the liquor entering the unit was calculated from,

$$(\text{solids entering}) \times 0.786 \frac{\text{Btu}}{\#F^\circ} \times (230-80)^\circ F$$

The sensible heat in the dry flue gas was calculated from

$$(\text{total dry flue gas}) \times 0.27 \frac{\text{Btu}}{\#^\circ F} \times (425-80)^\circ F$$

The heat content in the moisture in the flue gas was calculated from the enthalpy of superheated water vapor at 425°F and 3 psig. Thus,

$$(\text{total moisture in flue gas}) \times (1,252.7 - 48) \text{ Btu/lb}$$

The heat in smelt was assumed to be 580 Btu/lb of smelt in all cases.

The heat of reduction was taken to be 5,550 Btu/lb Na_2S.

The estimate of the heat of decarbonization was described in text.

Radiation losses were assumed to be 3% of the heating value for all cases.